

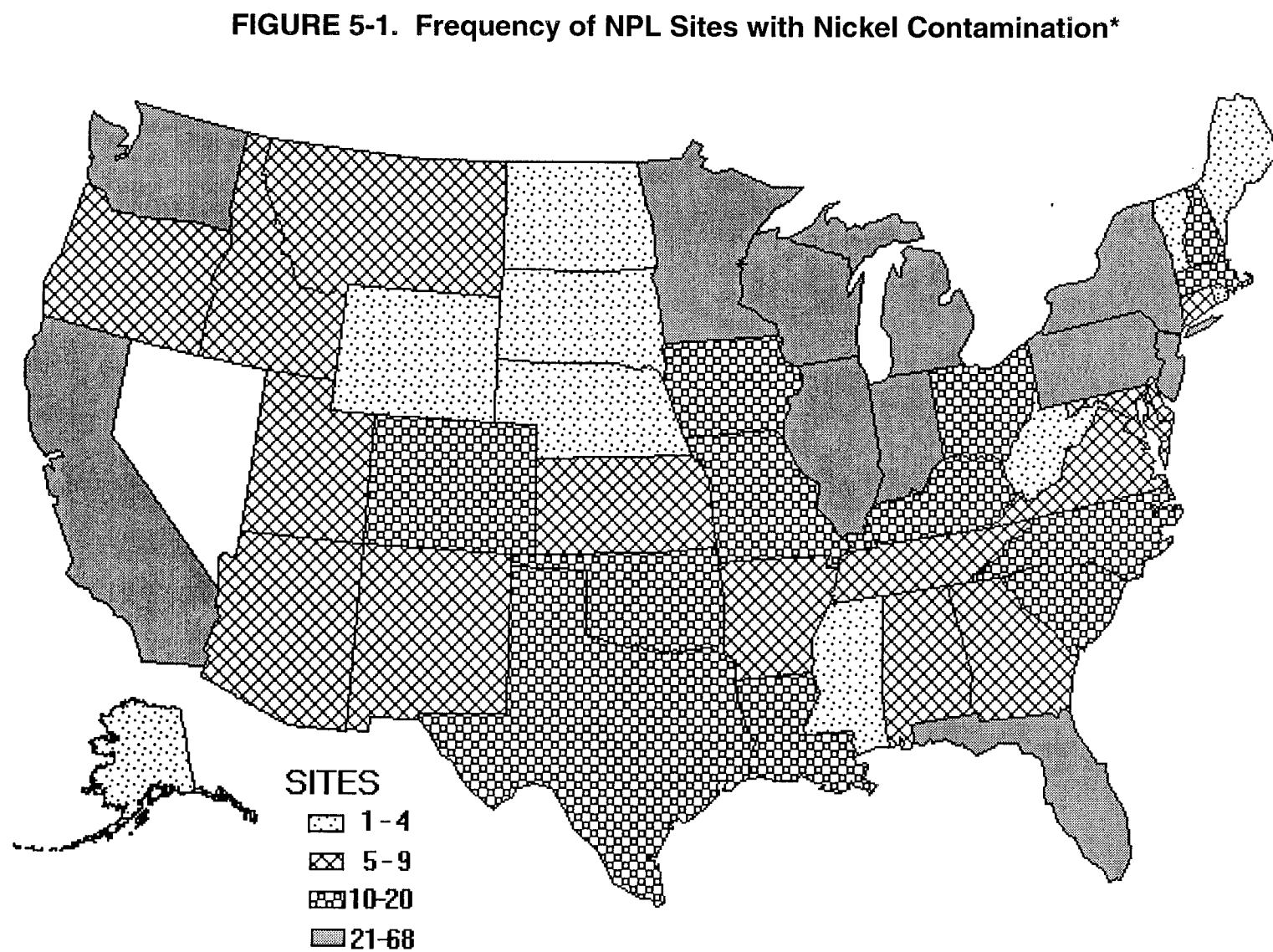
## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Nickel has been identified in at least 709 of the 1,430 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1996). However, the number of sites evaluated for nickel is not known. The frequency of these sites can be seen in Figure 5-1. Of these sites, 707 are located in the United States and 2 are located in the Commonwealth of Puerto Rico (not shown).

Nickel and its compounds are naturally present in the earth's crust, and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust, volcanoes, and vegetation each year. Five times that quantity is estimated to come from anthropogenic sources. The burning of residual and fuel oil is responsible for 62% of anthropogenic emissions, followed by nickel metal refining, municipal incineration, steel production, other nickel alloy production, and coal combustion (Bennett 1984; Schmidt and Andren 1980). Table 5-1 lists releases from facilities in the United States that produced, processed, or used nickel and its compounds in 1993, according to TRI (TR193 1995). These releases, which totaled 762,140 pounds (346,427 kg), were distributed as follows: 56% to land, 37.5% to air, 59% to water, and 1.5% to underground injection. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Nickel releases to the atmosphere are mainly in the form of aerosols that cover a broad spectrum of sizes. Particulates from power plants tend to be associated with smaller particles than those from smelters (Cahill 1989; Schroeder et al. 1987). Atmospheric aerosols are removed by gravitational settling and dry and wet deposition. Submicron particles may have atmospheric half-lives as long as 30 days (Schroeder et al. 1987). Monitoring data confirm that nickel can be transported far from its source (Pacyna and Ottar 1985). Nickel concentrations in air particulate matter in remote, rural, and U.S. urban areas are 0.01-60, 0.6-78, and 1-328 ng/m<sup>3</sup>, respectively (Schroeder et al. 1987).



\*Derived from HAZDAT 1996

**Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Nickel**

State <sup>b</sup>	Number of facilities	Range of reported amounts released in pounds per year <sup>a</sup>						
		Air	Water	Land	Underground Injection	Total environment <sup>c</sup>	POTW transfer	Off-site waste transfer
AL	38	0-622	0-340	0-8828	0	0-8942	0-1293	0-209405
AR	21	0-1581	0	0-15300	0	0-15300	0-250	0-98810
AZ	9	0-500	0	0-9000	0	0-9500	0-9	0-60490
CA	89	0-1300	0-3000	0-250	0	0-3000	0-250	0-130339
CO	20	0-750	0-200	0-250	0	0-750	0-250	0-87497
CT	49	0-500	0-5600	0-250	0	0-5600	0-250	0-482660
DE	4	0-3539	0-5	0-5	0	0-3549	0-19937	0-157695
FL	7	0-473	0-150	0-5	0-7800	0-7950	0-14	64-290000
GA	20	0-2255	0-250	0-1459	0	0-2255	0-250	0-1220000
IA	42	0-36915	0-250	0-250	0	0-36915	0-499	0-383620
ID	1	0	0	0	0	0	1	3
IL	97	0-3300	0-3200	0-14200	0	0-14265	0-2500	0-200000
IN	97	0-1641	0-250	0-46743	0-53	0-47493	0-499	0-1288000
KS	17	0-795	0-10	0-1600	0	0-1850	0-9	0-233500
KY	36	0-940	0-385	0-29286	0	0-29291	0-250	0-214320
LA	11	0-220	0-1100	0-62	0	0-1128	0-15	0-238078
MA	41	0-750	0-250	0-250	0	0-750	0-250	0-548468
MD	9	0-500	0-250	0	0	0-750	0-250	0-696422
ME	9	0-420	0-5	0-5	0	0-430	0-85	255-821976
MI	90	0-1939	0-750	0-8700	0-25	0-8811	0-1203	0-3819000
MN	27	0-2116	0-11	0	0	0-2116	0-5611	0-78000
MO	50	0-2172	0-1281	0-28552	0	0-28677	0-1276	0-94800
MS	11	0-1000	0-1	0-5	0	0-1000	0-250	0-154700

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**Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Nickel (continued)**

State <sup>b</sup>	Number of facilities	Range of reported amounts released in pounds per year <sup>a</sup>						
		Air	Water	Land	Underground injection	Total environment <sup>c</sup>	POTW transfer	Off-site waste transfer
MT	1	250	0	0	0	250	0	0
NC	42	0-500	0-60	0-750	0	0-755	0-250	0-783340
ND	2	0-20	0-7	0	0	0-27	0-3	250-92618
NE	12	0-500	0-250	0-2002	0	0-2502	0-2608	0-137750
NH	9	0-3300	0	0	0	0-3300	0-1	0-31523
NJ	20	0-475	0-23	0	0	0-475	0-1034	0-142860
NM	2	162-500	0-2	0-250	0	164-750	0-105	0-35332
NV	3	1-1100	0	0-210	0	30-1100	0	0-14356
NY	59	0-1523	0-280	0-3032	0	0-3111	0-750	0-750629
OH	163	0-8400	0-788	0-48000	0	0-56400	0-728	0-4014690
OK	30	0-607	0-3	0-250	0	0-620	0-750	0-407800
OR	13	0-500	0-250	0	0	0-505	0-250	0-99960
PA	148	0-2769	0-1335	0-91000	0-3200	0-94935	0-3079	0-2532342
PR	1	13	0	0	0	13	250	3662
RI	13	0-7	0	0	0	0-7	0-250	0-103641
SC	30	0-500	0-5	0-23	0	0-500	0-250	0-2121098
SD	3	5-250	0	0	0	5-250	0-250	0-9950
TN	48	0-500	0-250	0-20000	0	0-20002	0-274	0-225200
TX	75	0-6300	0-250	0-2270	0	0-6300	0-11000	0-234485
UT	13	0-3109	0	0-250	0	0-3109	0-1440	0-24416
VA	14	0-250	0-250	0-1596	0	0-1608	0-90	0-703000
VT	4	0-250	0	0-5	0	0-255	0-18	5-53783
WA	14	0-1119	0-980	0-2970	0	0-3950	0-32	0-48700

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**Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Nickel (continued)**

State <sup>b</sup>	Number of facilities	Range of reported amounts released in pounds per year <sup>a</sup>						
		Air	Water	Land	Underground injection	Total environment <sup>c</sup>	POTW transfer	Off-site waste transfer
WI	94	0-1035	0-750	0-3980	0	0-4235	0-650	0-449150
WV	9	0-14950	0-1146	0	0	0-16096	0-750	0-58500
WY	2	0-5	0	0	0	0-5	0-10	0-19478

Source: TRI93 1995

<sup>a</sup> Data in TRI are maximum amounts released by each facility.

<sup>b</sup> Post office state abbreviations used

<sup>c</sup> The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

POTW = publicly owned treatment works

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The form of nickel emitted to the atmosphere varies according to the type of source. Species associated with combustion, incineration, and metals smelting and refining are often complex nickel oxides, nickel sulfate, metallic nickel, and in more specialized industries, nickel silicate, nickel subsulfide, and nickel chloride (EPA 1985a).

The concentration of nickel in rain has been reported as  $\leq 1.5 \mu\text{g/L}$  (1.5 ppb). Concentrations of nickel in snow in Montreal, Canada, ranged from 2 to 300 ppb (Landsberger et al. 1983).

Nickel is a natural constituent of soil; levels vary widely depending on local geology and anthropogenic input. The typical concentrations of nickel reported in soil range from 4 to 80 ppm. Nickel may be transported into streams and waterways from the natural weathering of soil as well as from anthropogenic discharges and runoff. This nickel accumulates in sediment. Nickel levels in surface water are low. In some studies, nickel could not be detected in a large fraction of analyzed samples. Median nickel concentrations in rivers and lakes range from  $\approx 0.5$  to  $6 \mu\text{g/L}$ . Levels in groundwater appear to be similar to those in surface water. Levels in seawater are typically  $0.1$ - $0.5 \mu\text{g/L}$ .

The speciation and physicochemical state of nickel is important in considering its behavior in the environment and availability to biota. For example, the nickel incorporated in some mineral lattices may be inert and have no ecological significance. Most analytical methods for nickel do not distinguish the form of nickel; the total amount of nickel is reported, but the nature of the nickel compounds and whether they are adsorbed to other material is not known. This information, which is critical in determining nickel's lability and availability, is site specific. Therefore, it is impossible to predict nickel's environmental behavior on a general basis.

Little is known concerning the chemistry of nickel in the atmosphere. The probable species present in the atmosphere include soil minerals, nickel oxide, and nickel sulfate (Schmidt and Andren 1980). In aerobic waters at environmental pHs, the predominant form of nickel is the hexahydrate  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  ion (Richter and Theis 1980). Complexes with naturally occurring anions, such as  $\text{OH}^-$ ,  $\text{SO}_4^{=}$ , and  $\text{Cl}^-$ , are formed to a small degree. Complexes with hydroxyl radicals are more stable than those with sulfate, which in turn are more stable than those with chloride.  $\text{Ni}(\text{OH})_2^0$  becomes the dominant species above pH 9.5. In anaerobic systems, nickel sulfide forms if sulfur is present, and this limits the solubility of nickel. In soil, the most important sinks for nickel, other than soil

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minerals, are amorphous oxides of iron and manganese. The mobility of nickel in soil is site specific; pH is the primary factor affecting leachability. Mobility increases at low pH. At one well-studied site, the sulfate concentration and the surface area of soil iron oxides were also key factors affecting nickel adsorption (Richter and Theis 1980).

The general population is exposed to low levels of nickel in ambient air, water, and food. Exposure also occurs from smoking. The general population takes in most nickel through food. The average daily dietary nickel intake for U.S. diets was 150-168  $\mu\text{g}$  (Myron et al. 1978; Pennington and Jones 1987). These values agree with those from European studies. Typical average daily intakes of nickel from drinking water and air are 2 and 0.1-1  $\mu\text{g}$ , respectively. The highest general population intakes of nickel from water and air reported in Sudbury, Ontario, Canada, are 140 and 18  $\mu\text{g/day}$ , respectively. Other potential sources of nickel exposure are from contaminated intravenous fluids, dialysis, and leaching and corrosion of nickel from prostheses.

Occupational exposure to nickel may occur by dermal contact or by inhalation of aerosols, dusts, fumes, or mists containing nickel. Dermal contact may also occur with nickel solutions, such as those used in electroplating, nickel salts, and nickel metal or alloys. Nickel-containing dust may be ingested where poor work practices exist or poor personal hygiene is practiced. A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimates that 727,240 workers are potentially exposed to some form of nickel metal, alloys, salts, or inorganic nickel compounds in the United States (NIOSH 1990). The form of nickel these workers were probably exposed to and the level of exposure for different industries and operations were reviewed by Warner (1984) and IARC (1990).

Information on nickel exposure from hazardous waste sites is lacking. The most probable route of exposure from hazardous waste sites would be dermal contact, inhalation of dust, and ingestion of nickel-contaminated soil. Groundwater contamination may occur where the soil has a coarse texture and where acid waste, such as waste from plating industries, is discarded. People using this water may be exposed to high levels of nickel.

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### 5.2 RELEASES TO THE ENVIRONMENT

Most analytical methods for nickel in environmental samples do not distinguish between compounds of nickel or the nature of its binding to soil and particulate matter. It is generally impossible to say with certainty what forms of nickel are released from natural and anthropogenic sources, what forms are deposited or occur in environmental samples, and to what forms of nickel people are exposed. The form of nickel has important consequences as far as its transport, transformations, and bioavailability are concerned.

#### 5.2.1 Air

Nickel and its compounds are naturally present in the earth's crust, and releases to the atmosphere occur from natural processes such as windblown dust and volcanic eruption, as well as from anthropogenic activities. These latter releases are mainly in the form of aerosols. It is important to consider the background levels that are due to natural sources and distinguish them from levels that may result from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources each year (Bennett 1984; Schmidt and Andren 1980). The sources of this nickel are windblown dust, 56%; volcanoes, 29%; vegetation, 9%; forest fires, 2%; and meteoric dust, 2%. Anthropogenic sources of atmospheric nickel include nickel mining, smelting, refining, production of steel and other nickel-containing alloys, fossil fuel combustion, and waste incineration.

Emissions factors (i.e., kg of nickel emissions per unit consumption or production) have been estimated for various source categories, and these have been used to estimate worldwide emissions (Nriagu and Pacyna 1988). According to Schmidt and Andren (1980), annual anthropogenic emissions are estimated to contain 43 million kg of nickel (median value), five times the natural emission rate of 8.5 million kg/year. Nriagu and Pacyna (1988) estimate annual anthropogenic emissions as 55.6 million kg. The nickel emission factor for burning residual and fuel oil is estimated to be 0.03 kg/ton, yielding nickel emissions of 26.7 million kg/year or 62% of the total anthropogenic emissions (Schmidt and Andren 1980). The estimated contributions of other anthropogenic sources of nickel are nickel metal and refining, 17%; municipal incineration, 12%; steel production, 3%; other nickel-containing alloy production, 2%; and coal combustion, 2%



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(Bennett 1984; Schmidt and Andren 1980). Wood combustion is also an important source of nickel emissions (Nriagu and Pacyna 1988).

Table 5-1 lists the air releases from facilities in the United States that produce, process, or use nickel and its compounds, according to the 1993 TRI (TR193 1995). These releases, totaling 285,857 pounds (129,935 kg), constitute 37.5% of the environmental releases reported in the TRI. However, since the TRI does not include emissions from power plants and refuse and sludge incinerators, its estimate of U.S. nickel emissions is incomplete.

Deposition of metals around the large Copper Cliff smelter in Sudbury, Ontario, is a significant local problem. It is estimated that 42% of nickel particulates emitted from the 381-m stack are deposited within a 60-km radius of the smelter (Taylor and Crowder 1983). The Copper Cliff smelter, one of three large nickel sources in the Sudbury area, emits 592 pounds (269 kg) of nickel a day.

A typical, modern, coal-fired power plant emits  $\approx 25$   $\mu\text{g}$  nickel per Megajoule (MJ) of power produced, compared with 420  $\mu\text{g}/\text{MJ}$  for an oil-fired plant (Hasanen et al. 1986). The nickel concentration in stacks emissions from a modern coal-fired power plant with an electrostatic precipitator was 1.3  $\mu\text{g}/\text{m}^3$  (Lee et al. 1975). High-sulfur eastern coal has a higher nickel content than low-sulfur western coal, so power plants using eastern coal emit more nickel than those using western coal (QueHee et al. 1982).

From a public health point of view, the concentration of nickel associated with small particles that can be inhaled into the lungs is of greatest concern. The nickel content of aerosols from power plant emissions is not strongly correlated with particle size (Hansen and Fisher 1980). In one modern coal plant, 53% and 32% of nickel in emissions were associated with particles  $<3$  and  $<1.5$   $\mu\text{m}$  in diameter, respectively (Sabbioni et al. 1984). Other studies found that only 17-22% of nickel emissions from coal-fired power plants were associated with particles of  $>2$   $\mu\text{m}$ , and that the mass medium diameter (MMD) of nickel-containing particles from a plant with pollution control devices was 5.4  $\mu\text{m}$  (Gladney et al. 1978; Lee et al. 1975). In one study, 40% of the nickel in coal fly ash was adsorbed on the surface of the particles rather than being embedded in the aluminosilicate matrix (Hansen and Fisher 1980). Surface-adsorbed nickel would be more available than embedded nickel.

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Nickel emissions from municipal incinerators depend on the nickel content of the refuse and the design and operation of the incinerator. By comparing the nickel content of particles emitted from two municipal incinerators in Washington, DC, with that of atmospheric particulate matter, Greenberg et al. (1978) concluded that refuse incineration is not a major source of nickel in the Washington area. The average nickel concentration in suspended particles from these incinerators is 170 and 200 ppm. Nickel is not primarily associated with very fine or coarse particles. In tests performed under the Canadian National Incinerator Testing and Evaluation Program, 1.0 g nickel/ton refuse was emitted under normal operating conditions; when the combustion chamber operated at low and high combustion temperatures, nickel emissions increased to  $\leq 2.2$  g nickel/ton (Hay et al. 1986). These emissions can be compared with a factor of 0.33 g nickel/ton refuse obtained in a European study (Pacyna 1984). The European study also obtained an emission factor of 1.0 g nickel/ton for sewage sludge incineration.

An increase in nickel emissions over presettlement levels was assessed by dating and analyzing peat cores from a fen located in northern Indiana, which is downwind from the city of Chicago and the industrial complexes of Gary and East Chicago, areas that contain a large steel mill and a coal-fired power plant. The peak accumulation rate was 7.73 mg nickel/m<sup>2</sup>/year for 1970-1973, a factor of 21 greater than the accumulation rate in presettlement times (A.D. 1339-1656) (Cole et al. 1990).

Some work has been performed to determine the species of nickel present in air emissions from different source categories (EPA 1985a). This has been determined from analyses of dust by x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray analysis or by an assessment of the reactions and transformations possible for the material present and the process conditions. Nickel resulting from oil combustion is primarily nickel sulfate with lesser amounts of complex metal oxides and nickel oxide. Approximately 90% of nickel in fly ash from coal combustion consists of complex (primarily iron) oxides. Nickel silicate and iron-nickel oxides would be expected from the mining and smelting of lateritic nickel ore, whereas nickel matte refining would produce nickel subsulfide and metallic nickel. The primary nickel species from secondary nickel smelting and steel and nickel alloys production is iron-nickel oxide.

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### 5.2.2 Water

Nickel is a natural constituent of soil and is transported into streams and waterways in runoff either from natural weathering or from disturbed soil. Much of this nickel is associated with particulate matter. Nickel also enters bodies of water through atmospheric deposition.

Emission factors have been estimated for the release of trace metals to water from various source categories and these have been used to estimate inputs of these metals into the aquatic ecosystem. The global anthropogenic input of nickel into the aquatic ecosystem for 1983 is estimated to be between 33 and 194 million kg/year with a median value of 113 million kg/year (Nriagu and Pacyna 1988).

Table 5-1 presents releases of nickel to water from facilities that produced, processed, and used nickel in 1993 in the United States. These releases, totaling 38,093 (17,315 kg) pounds of nickel and nickel compounds in 1993, constitute 5% of environmental releases reported to TRI (TR193 1995). The TRI data listed in Table 5-1 should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

A survey of raw and treated waste water from 20 industrial categories indicated that nickel is commonly found in some waste waters. Those industries with mean effluent levels of  $>1,000$   $\mu\text{g/L}$  in raw waste water were inorganic chemicals manufacturing (20,000  $\mu\text{g/L}$ ), iron and steel manufacturing (1,700  $\mu\text{g/L}$ ), battery manufacturing (6,700  $\mu\text{g/L}$ ), coil coating (1,400  $\mu\text{g/L}$ ), metal finishing (26,000  $\mu\text{g/L}$ ), porcelain enameling (19,000  $\mu\text{g/L}$ ), nonferrous metal manufacturing ( $<91,000$   $\mu\text{g/L}$ ), and steam electric power plants (95,000  $\mu\text{g/L}$ ) (EPA 1981). Those industries with mean effluent levels  $>1,000$   $\mu\text{g/L}$  in treated waste water were porcelain enameling (14,000  $\mu\text{g/L}$ ) and nonferrous metal manufacturing (14,000  $\mu\text{g/L}$ ) (EPA 1981). The maximum levels in treated discharges from these industries were 67,000 and 310,000  $\mu\text{g/L}$ , respectively. In addition, four other industrial categories had maximum concentrations in treated discharges  $>1,000$   $\mu\text{g/L}$ . These were inorganic chemicals manufacturing (1,400  $\mu\text{g/L}$ ), iron and steel manufacturing (7,800  $\mu\text{g/L}$ ), aluminum forming (20,000  $\mu\text{g/L}$ ), and paint and ink formulation (80,000  $\mu\text{g/L}$ ).

Domestic waste water is the major anthropogenic source of nickel in waterways (Nriagu and Pacyna 1988). Concentrations of nickel in influents to 203 municipal waste-water treatment plants

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(9,461 observations) ranged from 2 to 111,400  $\mu\text{g/L}$ ; the median value was  $\approx 300$   $\mu\text{g/L}$  (Minear et al. 1981). Concentrations in treated effluents were not reported. However, nickel may be removed by chemical precipitation or coagulation treatment in publicly owned treatment works, which reduces nickel releases (EPA 1981).

Effluent water generated from mining and smelting operations comes from seepage, runoff from tailing piles, or from utility water used for mine operations. These discharges consist mostly of less-soluble silicates and sulfides and readily settle out. Tailing effluents from sulfidic ores are acidic due to the bacterial generation of sulfuric acid from the sulfidic minerals in the tailings, and very high concentrations of soluble nickel sulfate may be released. Tailing waters from the Onaping and Sudbury areas of Ontario, Canada, have an average nickel content of 42,500  $\mu\text{g/L}$ , a factor of 8,300 greater than that found in river water (Mann et al. 1989). Since there is presently no nickel mining of sulfidic ore in the United States, nickel-containing waste water is not generated by this activity. However, past nickel mining may have contributed to nickel entering our waterways and accumulating in sediment. Old tailing piles may contribute to runoff for decades.

In the EPA-sponsored National Urban Runoff Program, in which 86 samples of runoff from 15 cities throughout the United States were analyzed, nickel was found in 48% of runoff samples, at concentrations of 1-182  $\mu\text{g/L}$  (Cole et al. 1984). The geometric mean nickel concentration in runoff water from the cities studied was between 5.8 and 19.1  $\mu\text{g/L}$ . The major source of this nickel is believed to be gasoline.

One of the potentially dangerous sources of chemical release at waste sites is landfill leachate. In a study that looked at leachate from three municipal landfills in New Brunswick, Canada, the results were conflicting. Average nickel concentrations in the three leachates (control) were 28 (45)  $\mu\text{g/L}$ , 33 (not detectable)  $\mu\text{g/L}$ , and 41 (23)  $\mu\text{g/L}$  (Cyr et al. 1987). Sediment at three sites below the leachate outfalls contained 11.9, 37.4, and 71.2 ppm of nickel (dry weight).

### 5.2.3 Soil

Most of the nickel released to the environment is released to land. Emission factors for nickel released to soil have been estimated for various industries (Nriagu and Pacyna 1988). These factors can be used to estimate industrial nickel releases to land. Excluding mining and smelting releases

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to land, 66% of estimated anthropogenic environmental releases or 325 million kg/year (median) are to soil (Nriagu and Pacyna 1988). Some important sources of nickel released to soil are coal fly ash and bottom ash, waste from metal manufacturing, commercial waste, atmospheric fallout, urban refuse, and sewage sludge. Table 5-1, which shows the range of releases from industries listed in the TRI that produce, process, or use nickel, indicates that the bulk of nickel and nickel compounds is released to land. In 1993, 56% of these releases or 427,112 pounds (194,142 kg) were to land (TR193 1995). Underground injection accounted for 1.5% or 11,078 pounds (5,035 kg) of nickel and nickel compounds released to the environment (TR193 1995). Since not all facilities are required to report to the TRI, the list of facilities releasing nickel to land is not complete.

### 5.3 ENVIRONMENTAL FATE

It is not always possible to separate the environmental fate processes relating to transport and partitioning from those relating to transformation for a metal and its various compounds and complexes. Because of analytical limitations, investigators rarely identify the form of a metal present in the environment. A change in the transport or partitioning of a metal may result from a transformation. For example, complexation may result in enhanced mobility, while the formation of a less-soluble sulfide would decrease its mobility in water. Adsorption may be the result of strong bonds being formed (transformation) as well as weak ones. Separating data relating to strong and weak adsorption in different sections is awkward and may not always be possible. Section 5.3.1 covers deposition and general adsorption of nickel, and Section 5.3.2 examines areas of environmental fate in which speciation occurs.

#### 5.3.1 Transport and Partitioning

Nickel is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is dispersed by wind and removed by gravitational settling (sedimentation), dry deposition (inertial impaction characterized by a deposition velocity), washout by rain (attachment to droplets within clouds), and rainout (scrubbing action below clouds) (Schroeder et al. 1987). The removal rate and distance traveled from the source depends on source characteristics (e.g., stack height), particle size and density, and meteorological conditions.

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Gravitational settling governs the removal of large particles ( $>5\ \mu\text{m}$ ), whereas smaller particles are removed by other forms of dry and wet deposition. The partitioning between dry and wet deposition depends on the intensity and duration of precipitation, the element in question and its form in the particulate matter, and particle size. The importance of wet deposition relative to dry deposition generally increases with decreasing particle size. Removal of coarse particles may occur in a matter of hours. Very small particles may have an atmospheric half-life as long as 30 days and may, therefore, be transported over long distances (Schroeder et al. 1987). Evidence for the long-range transport of nickel is provided by the fact that emission sources in North America, Greenland, and Europe are responsible for elevated atmospheric nickel concentrations in the Norwegian arctic during both the summer and winter (Pacyna and Ottar 1985).

Available studies indicate that nickel is broadly distributed among aerosol size groups. A study to determine the size distribution of nickel-containing aerosols in clean, marine air was performed on an island in the German Bight (Stoessel and Michaelis 1986). The concentration of nickel in six size fractions increased with decreasing size from  $\approx 0.3\ \text{ng}/\text{m}^3$  for particles  $>7.2\ \mu\text{m}$  to  $\approx 1.5\ \mu\text{g}/\text{m}^3$  for particles  $<0.5\ \mu\text{m}$ . Experiments in Ontario showed that nickel is associated with relatively large particles,  $5.6 \pm 2.4\ \text{pm}$  (Chan et al. 1986). A 1970 National Air Surveillance Network study of the average nickel size distribution in six American cities indicated that the MMD is  $\approx 1.0\ \mu\text{m}$  in all six cities. Although the sampling procedure used in this study may have underestimated large particles (Davidson 1980), it represents one of the few studies involving the size distribution of nickel aerosols in U.S. cities.

Metal deposition is characterized by large temporal and spatial variability. Deposition can be associated with precipitation (wet deposition) or result from processes such as gravitational settling of dust (dry deposition). Estimated nickel deposition rates range from 0.01 to 0.5 kg/hectare-year ( $1\text{--}50\ \text{mg}/\text{m}^2\text{-year}$ ) and from 0.1 to 5.95 kg/hectare-year ( $10\text{--}595\ \text{mg}/\text{m}^2\text{-year}$ ) in rural and urban areas, respectively (Schroeder et al. 1987). Nickel deposition from 1980 to 1981 in an industrial area of England where a number of ferrous and nonferrous metal smelting and manufacturing works were concentrated had a mean value of  $8,800\ \text{ng}/\text{cm}^2\text{-year}$  ( $88\ \text{mg}/\text{m}^2\text{-year}$ ), a factor of 8-25 above nonurban deposition rates (Pattenden et al. 1982). Wet deposition accounted for half of the deposition. Eighty-one percent of the nickel in rain was dissolved. Schroeder et al. (1987) reported the same percent of dry to wet deposition for nickel, whereas Chan et al. (1986) found that 2.2 times as much wet deposition as dry deposition occurred in Ontario in 1982 with little

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variability in the ratio across the province. The mean dry deposition rates for southern, central, and northern Ontario in 1982 were 0.25, 0.28, and 0.18 mg m<sup>-2</sup>-year, respectively. In southern Ontario, Canada, where the average concentration of nickel in rain was 0.557 ppb during 1982, 0.5 mg of nickel was deposited annually per square meter as a result of wet deposition (Chan et al. 1986). For central and northern Ontario, the mean concentrations of nickel in rain were 0.613 and 0.606 ppb, respectively, and the annual wet depositions averaged 0.5 and 0.4 mg/m<sup>2</sup>.

The fate of heavy metals in aquatic systems depends on partitioning between soluble and particulate solid phases. Adsorption, precipitation, coprecipitation, and complexation are processes that affect partitioning. These same processes, which are influenced by pH, redox potential, the ionic strength of the water, the concentration of complexing ions, and the metal concentration and type, affect the adsorption of heavy metals to soil (Richter and Theis 1980).

Much of the nickel released into waterways as runoff is associated with particulate matter; it is transported and settles out in areas of active sedimentation such as the mouth of a river. Additionally, when a river feeds into an estuary, the salinity changes may affect absorptivity due to complexation and competition for binding sites (Bowman et al. 1981). During a 4-month study of Lake Onondaga in Syracuse, New York, 36% of the nickel in the lake was lost to sediment (Young et al. 1982). Seventy-five percent of the nickel load into the polluted lake was soluble and remained in the lake. Nickel is strongly adsorbed at mineral surfaces such as oxides and hydrous oxides of iron, manganese, and aluminum (Evans 1989; Rai and Zachara 1984). Such adsorption plays an important role in controlling the concentration of nickel in natural waters.

Nickel is strongly adsorbed by soil, although to a lesser degree than lead, copper, and zinc (Rai and Zachara 1984). There are many adsorbing species in soil, and many factors affect the extent to which nickel is adsorbed, so the adsorption of nickel by soil is site specific. Soil properties such as texture, bulk density, pH, organic matter, the type and amount of clay minerals, and certain hydroxides influence the retention and release of metals by soil (Richter and Theis 1980).

Amorphous oxides of iron and manganese, and to a lesser extent clay minerals, are the most important adsorbents in soil. In alkaline soils, adsorption may be irreversible (Rai and Zachara 1984), which limits nickel's availability and mobility in these soils. Cations such as Ca<sup>+2</sup> and Mg<sup>+2</sup> have been reported to reduce adsorption due to competition for binding sites, whereas anions like

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sulfate reduce adsorption as a result of complexation. Nickel adsorption depends strongly on pH. For each mole of nickel adsorbed by iron and manganese oxide,  $\approx 1$ -1.5 moles of hydrogen ions are released (Rai and Zachara 1984). For aluminum oxide, as many as 2.3 moles  $H^+$  are released. Mustafa and Haq (1988) found that the adsorption of nickel onto iron oxide at pH 7.0 was rapid and increased with increasing temperature. They found that two hydrogen ions are released into a solution when nickel is adsorbed. These studies indicate that while  $Ni^{+2}$  is the predominant species in solution,  $NiOH^+$  is preferentially adsorbed, and that both mono- and bidentate complexes may be formed with the iron/manganese/aluminum oxides.

Batch equilibrium studies were performed using seven soils and sediments spiked with varying concentrations of nickel to assess the potential mobility of nickel in contaminated subsoil (LaBauve et al. 1988). The range of Freundlich parameters  $K(1/n)$ , adsorption constants, ranged from 739 (0.92) to 6,112 (0.87). One-, two-, and three-parameter models were used to evaluate the relation of soil properties and nickel retention. In the one-parameter model, pH was the best predictor. Cation exchange capacity (CEC) and iron oxide were the best predictors in the twoparameter models, and CEC, iron oxide, and percent clay were the best predictors in the threeparameter models. Nickel was more mobile in the soils than lead, cadmium, and zinc. The retention of nickel to two of the test subsoils diminished in the presence of synthetic landfill leachate, possibly because of complex formation. In another study in which batch adsorption experiments were conducted with a mixture of cadmium, cobalt, nickel, and zinc, and 38 different agricultural soils, taken from three depths at 13 sites, the adsorption constants ranged from 10 to 1,000 L/kg (Anderson and Christensen 1988). Soil pH, and to a lesser extent clay content and the amount of hydrous iron and manganese oxides, most influenced nickel sorption.

In 12 New Mexican soils from agricultural areas and potential chemical waste disposal sites, Freundlich parameters  $K(1/n)$  ranged from 8.23 to 650 (0.87-1.18); the median  $K$  was 388 (Bowman et al. 1981). The soil with the  $K$  of 8.23 was essentially unweathered rock that was not expected to have good adsorbing properties. The study concluded that most soils have an extremely high affinity for nickel and that once sorbed, nickel is difficult to desorb, which indicates covalent bond formation. Sadiq and Enfield (1984b) observed nickel ferrite formation following adsorption. Bowman et al. (1981) found that when nickel levels were  $>10$  ppm, adsorption decreased. High concentrations of chloride decreased adsorption, but not as much as calcium ions, which indicates that calcium competition for sorbing sites is more important than chloride



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complexation for reducing adsorption. The presence of complexing agents, such as EDTA, dramatically lowers nickel adsorption, which has important implications at waste disposal sites if liquid nickel waste containing chelating agents is released to soil. Chelating agents that are added to soil containing adsorbed nickel appear to have a lesser effect.

The capacity of soil to remove nickel and the nature of the bound nickel were evaluated for 10 mineral and 3 organic soils from the southeastern United States (King 1988). Some soil samples were taken from the subsoil as well as the surface. The amount of adsorbed nickel ranged from 13% to 95%; the low value was found in subsoil, and the high value was found in soil high in organic matter. When extracted with potassium chloride, 5-87% of the nickel was nonexchangeable. Soil pH was the most important factor affecting sorbed and nonexchangeable nickel in all soil horizons. Both King (1988) and Tyler and McBride (1982) found much stronger nickel adsorptivity in organic soil than in mineral soils. Adsorption was improved by the quality and quantity of humus in the soil (Hargitai 1989). Nickel was enriched in humic and fulvic acids from Lake Ontario sediment (Nriagu and Coker 1980). It was estimated that 5-10% of the nickel in this sediment was bound to organic matter.

Nickel (Ni II) is poorly removed from waste water in the activated sludge process because of its high solubility (Stephenson et al. 1987). Only 30-40% of nickel was removed in a pilot activated sludge plant. Nickel removal in activated sludge plants is best correlated with effluent suspended solids (Kempton et al. 1987). Nickel is predominantly soluble in the effluent.

In order to evaluate the potential of elements to leach from land-spread sewage sludge, Gerritse et al. (1982) studied the adsorption of elements to sandy and sandy loam top soils from water, salt solutions, and sludge solutions. They used metal levels that occurred in the solution phase of sewage sludge, 100-1,000 ppb in the case of nickel. The results indicated that nickel is fairly mobile in these soils; the adsorption constants were  $\approx 10$ -100 in the sandy soil and a factor of  $\approx 10$  higher in the sandy loam soil. The presence of sludge increases the mobility of nickel, particularly in the sandy loam soil, which may be because of complexation with dissolved organic compounds or increased ionic strength (Gerritse et al. 1982). However, land application of nickel-contaminated sludge did not give rise to increased levels of nickel in groundwater (Demirjian et al. 1984). Higher doses and repeated application of nickel-containing sewage sludge did not result in a proportional increase in nickel mobility (Hargitai 1989).

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As part of EPA's National Runoff Program in Fresno, California, the soil water and groundwater at depths  $\leq 26$  m beneath five urban runoff retention/recharge basins were monitored during a 2-year study (Nightingale 1987). The results indicated that there were no significant downward movements of nickel with the recharge water.

Saline sediments from estuaries often contain pyrite and other readily oxidizable sulfur compounds. When these sediments are oxidized, such as when dredged sediment is exposed to oxygen, sulfuric acid may be produced which may overwhelm the buffering capacity of the sediment, lower the pH (to pH 3.1 in a laboratory experiment), and dissolve the ferric oxides and hydroxides that entrap heavy metals (DeLaune and Smith 1985). As a result, significant amounts of nickel may be released from the dredged sediments. An analogous pH decrease following exposure to oxygen was not observed in freshwater sediment.

Nickel is not accumulated in significant amounts by aquatic organisms (Birge and Black 1980; Zaroogian and Johnson 1984). The concentration of nickel in a major carnivorous fish in New York State, the lake trout, was the lowest, and the concentration did not increase appreciably with the age of the fish (Birge and Black 1980). The mean bioconcentration factor (BCF) for three carnivorous fish was 36. The concentration of nickel in mussels and oysters treated with 5  $\mu\text{g}$  nickel/kg of seawater for 12 weeks averaged 9.62 and 12.96  $\mu\text{g}$  nickel/g, respectively, on a dry weight basis (Zaroogian and Johnson 1984). When these data are adjusted for controls and the nickel concentration in tissue is expressed on a wet weight basis, the BCF for the mussels and oysters is  $\approx 100$ . After 2 weeks in flowing seawater, 58% and 38% of the tissue nickel was lost from the mussel and oyster, respectively. No significant loss of nickel occurred during the remainder of the 28-week depuration period. The content of acid volatile sulfide (AVS) in sediment helps determine the bioavailability of metals (Ankley et al. 1991). In studies of nickel and cadmium, the metals were toxic to an amphipod (*Hyallela azteca*) and an oligochaete (*Lumbriculus variegatus*) when the extracted metals/AVS ratio was greater than 1.

Two studies concerning levels in voles and rabbits living on sludge-amended land did not indicate any accumulation of nickel in these herbivores or in the plants they fed upon (Alberici et al. 1989; Dressler et al. 1986). The lack of significant bioaccumulation of nickel in aquatic organisms, voles, and rabbits indicates that nickel is not biomagnified in the food chain.

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### 5.3.2 Transformation and Degradation

Analytical methods do not generally allow identification of the precise form of nickel present in environmental samples or an assessment of the transformations that may occur. Sequential extraction techniques are sometimes employed to determine how tightly nickel is bound to particles or in environmental matrices. Using different and progressively stronger extracting agents, the fractions of a sample that are exchangeable, adsorbed, easily reducible, moderately reducible, or organically bound carbonates, sulfides, and residual can be determined (Rudd et al. 1988; Rybicka 1989).

#### 5.3.2.1 Air

Little is known about the chemical forms and physical and chemical transformations of trace elements in the atmosphere primarily because analytical methods provide information concerning the metal content rather than the specific compounds or species. In the absence of specific information, it is generally assumed that elements of anthropogenic origin, especially those emanating from combustion sources are present as the oxide, and nickel oxide has been identified in industrial emissions (Schroeder et al. 1987). Windblown dust particles may contain nickel in mineral species, which often contain nickel as the sulfide. Increases in the concentration of nickel in Sequoia National Park in California during rain coming from the south correlated with sharp increases in sulfur (Cahill 1989). Nickel sulfate is a probable atmospheric species resulting from the oxidation of nickel in the presence of sulfur dioxide (Schmidt and Andren 1980).

The form of nickel in particles from different industries varies. The mineralogical composition, chemical content, and form of dusts from nine industries in Cracow, Poland, were examined (Rybicka 1989). The chemical form of a particle-associated heavy metal that was assessed by a five-step extraction scheme classified the metal as exchangeable, easily reducible (manganese oxides, partly amorphous iron oxyhydrates and carbonates), moderately reducible (amorphous and poorly crystallized iron oxyhydrates), organically bound or sulfidic, and residual. Dusts from power plants had a silicate characteristic with quartz and mullite predominant. Approximately 90% of the nickel from these facilities was in the residual fraction. Only 40-60% of the nickel from metallurgical, chemical, and cement plants was in the residual fraction. Essentially none of the nickel from any of the industries was in an organic/sulfidic fraction. Dusts from metallurgical, chemical, and

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cement plants contained between 0% and 10% (typically 5%) of the nickel in the relatively mobile, cation-exchangeable fraction. Thirty percent of the nickel in dust from a slag processing facility was in this form.

### 5.3.2.2 Water

In natural waters, nickel primarily exists as the hexahydrate. While nickel forms strong, soluble complexes with  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ , these species are minor compared with hydrated  $\text{Ni}^{2+}$  in surface water and groundwater with  $\text{pH} < 9$  (Rai and Zachara 1984). Under anaerobic conditions, such as may exist in deep groundwater, nickel sulfide would control aqueous nickel concentrations to low levels.

Precipitation can remove soluble nickel from water. In aerobic waters, nickel ferrite is the most stable compound (Rai and Zachara 1984). Nickel may also be removed by coprecipitation with hydrous iron and manganese oxides. Nickel removed by precipitation and coprecipitation settles into the sediment.

Nickel in sediment may be strongly bound or present in a removable form. A metal's form in soil or sediment and its availability are determined by measuring the extractability of the metal with different solvents. Sediment samples from western Lake Ontario were analyzed in regard to the compositional associations of nickel by a series of sequential extractions (Poulton et al. 1988). The mean nickel percentages in the various fractions were as follows: exchangeable,  $0.7 \pm 1.4$ ; carbonate, 0.0; iron or manganese oxide-bound, 0.0; organic-bound,  $7.4 \pm 4.1$ ; and residual,  $91.9 \pm 4.5$ . The nickel concentration in 450 uncontaminated estuarine and coastal marine sites in the southeastern United States covaried significantly with the aluminum concentration, suggesting that natural aluminosilicates are the dominant natural metal-bearing phase in some aquatic systems (Windom et al. 1989). In 13 random samples of bottom sediment from the highly industrialized Meuse River in The Netherlands, between 0% and 88% (median 33%) of the nickel was removable at low pH showing the great variability of nickel to adsorb to sediments (Mouvet and Bourg 1983).

Nickel removed by coprecipitation can be remobilized by microbial action under anaerobic conditions (Francis and Dodge 1990). Remobilization results from enzymatic reductive dissolution of iron with subsequent release of coprecipitated metals. A lowering of pH as a result of

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enzymatic reactions may indirectly enhance the dissolution of nickel. Experiments using mixed precipitates with goethite ( $\alpha$ -FeOOH) indicated that a *Clostridium* species released 55% of the coprecipitated nickel after 40 hours. Similarly, precipitated nickel sulfides in sediment can be mobilized through sulfur oxidation by *Thiobacilli* (Wood 1987). In this case, the oxidized sulfur may produce  $\text{H}_2\text{SO}_4$  and decrease the pH.

### 5.3.2.3 Sediment and Soil

An analysis of the thermodynamic stability models of various nickel minerals and solution species indicates that nickel ferrite is the solid species that will most likely precipitate in soils (Sadiq and Enfield 1984a). Experiments on 21 mineral soils supported its formation in soil suspensions following nickel adsorption (Sadiq and Enfield 1984b). The formation of nickel aluminate, phosphate, or silicate was not significant.  $\text{Ni}^{2+}$  and  $\text{Ni}(\text{OH})^+$  are major components of the soil solution in alkaline soils. In acid soils, the predominant solution species will probably be  $\text{Ni}^{2+}$ ,  $\text{NiSO}_4^0$ , and  $\text{NiHPO}_4^0$  (Sadiq and Enfield 1984a).

A large percentage of nickel in sewage sludges exists in a form that is easily released from the solid matrix (Rudd et al. 1988). Although the availability of nickel to plants grown in sludgeamended soil is correlated with soil-solution nickel, it is only significantly correlated with DTPAextractable nickel (Adams and Kissel 1989).

## 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

### 5.4.1 Air

The nickel concentration in particulate matter in the U.S. atmosphere ranged from 0.01 to 60, 0.6 to 78, and 1 to 328  $\text{ng}/\text{m}^3$  in remote, rural, and urban areas, respectively (Schroeder et al, 1987). Annual mean nickel concentrations in 11 Canadian cities measured during 1987-1990 ranged from 1 to 20  $\text{ng}/\text{m}^3$ , while at a rural location the mean nickel concentration was 1  $\text{ng}/\text{m}^3$  (CEPA 1994). Annual average nickel concentrations at three remote sites in the arctic region of Canada ranged from 0.14 to 0.45  $\text{ng}/\text{m}^3$  (Barrie and Hoff 1985). Levels of nickel and other anthropogenic species peaked during January and February, possibly indicating the significance of combustion sources. Nickel levels in the air at three native villages in northern Alberta, Canada, were  $0.779 \pm 0.774$ ,

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4.9729.2, and  $1.1 \pm 0.57 \text{ ng/m}^3$ , indicating that air concentrations of nickel can be highly variable (Moon et al. 1988).

According to the EPA's National Air Surveillance Network (NASN) report for 1977, 1978, and 1979, median nickel concentrations were below the detection limit for urban and nonurban samples except for 1978; during 1978, the urban median was  $6 \text{ ng/m}^3$  (Evans et al. 1984). The detection limit for inductively-coupled-plasma atomic emission spectroscopy (ICP-AES), the method used in the EPA study, was  $\approx 1 \text{ ng/m}^3$  (EPA 1986a; Evans et al. 1984). In the EPA study, 10,769 urban samples and 1,402 nonurban 24-hour air samples were analyzed. Five percent of the urban samples were  $>33$ ,  $32$ , and  $30 \text{ ng nickel/m}^3$  for 1977, 1978, and 1979, respectively; 5% of the nonurban samples were  $>10$ ,  $10$ , and  $6 \text{ ng/m}^3$ , respectively, for these 3 years. Ninety-nine percent of the urban and nonurban samples for these 3 years did not exceed  $68$  and  $52 \text{ ng/m}^3$ , respectively (Evans et al. 1984). Combined urban and nonurban measurements for the 99th percentile from the NASN (1977-1979) and its successor, the National Air Monitoring Filter Sites (NAMFS) (1980-1982), showed a sharp decline from  $62$  and  $67 \text{ ng/m}^3$  in 1977 and 1978 to  $23$  and  $30 \text{ ng/m}^3$  in 1981 and 1982. Mean levels for the combined urban and nonurban sites over the 6-year period ranged from  $7$  to  $12 \text{ ng/m}^3$  (EPA 1986a). According to the NASN data for 1965-1968, the average atmospheric nickel concentration in the air of 28 cities ranged from  $3$  to  $90 \text{ ng/m}^3$ , with an overall average of  $26 \text{ ng/m}^3$  (NAS 1975). These data suggest that atmospheric nickel concentrations in the United States have been declining. No reason for this downward trend was suggested (EPA 1986a).

The most intensive study of the nickel concentration in the United States was the result of analyzing air samples collected during 1968-1971 for use in a lead survey (Saltzman et al. 1985). This study is significant because numerous sites in four cities were analyzed continuously over 1 year and analyzed by a single, highly experienced laboratory. Samples (4,579) from 33 sites in Chicago, Houston, New York, and Washington, DC, were analyzed for nickel resulting in respective geometric mean nickel concentrations of  $18$ ,  $15$ ,  $42$ , and  $23 \text{ ng/m}^3$ . The results for Washington, DC, are in basic agreement with more recent results (Kowalczyk et al. 1982). In this study, 24-hour samples collected at 10 locations yielded average nickel concentrations ranging from  $5.7$  to  $35 \text{ ng/m}^3$ , with a mean concentration of  $17 \text{ ng/m}^3$ . The two major contributing sources are believed to be oil and coal combustion. The enrichment factor for nickel over crustal levels in 29 cities is  $11$  (Gladney et al. 1984). An enrichment factor considerably greater than  $1$  indicates that the

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source of an element is anthropogenic. In Houston, the average concentration of nickel in both the fine (0.1-2.5  $\mu\text{m}$ ) aerosols and those  $>2.5 \mu\text{m}$  was  $4\pm 1 \text{ ng/m}^3$  (Johnson et al. 1984).

As part of the Airborne Toxic Element and Organic Substances project for determining patterns of toxic elements in different settings, three urban areas (Camden, Elizabeth, and Newark) and one rural site (Ringwood) in New Jersey were studied during two summers and winters between 1981 and 1983 (Lioy et al. 1987). Each site was sampled every 24 hours for 39 consecutive days. The geometric mean nickel concentrations were 8.0-34.0, 5.0-28.0, 10.0-27.0, and 5.0-13.0  $\text{ng/m}^3$  for Camden, Elizabeth, Newark, and Ringwood, respectively. The nickel levels measured in the industrial urban areas may be compared to the arithmetic mean values reported in the National Air Surveillance survey (9.6-11.0  $\text{ng/m}^3$ ) for 1977-1979 (Evans et al. 1984). Summer and winter maxima in the three urban areas ranged from 24.0 to 39.0 and from 81.0 to 112.0  $\text{ng/m}^3$ , respectively, and 22.0 and 32.0  $\text{ng/m}^3$ , respectively, for Ringwood.

The first and second highest annual average nickel concentrations in the air in Texas between 1978 and 1982, according to the Texas Air Control Board, were 49 and 34  $\text{ng/m}^3$  at Port Arthur and Beaumont, respectively (Wiersema et al. 1984). The statewide 1978-1982 average was 1  $\text{ng/m}^3$ . Mean nickel levels showed relatively little geographic variation in Ontario where concentrations in southern, central, and northern Ontario were 0.81, 0.91, and 0.58  $\text{ng/m}^3$ , respectively (Chan et al. 1986).

### 5.4.2 Water

Surface water contains low nickel levels. The concentration in seawater ranges from 100 to 3,000  $\text{ng nickel/L}$ . Higher levels are found in deeper waters than in surface water (Mart et al. 1984; Sunderman 1986; van Geen et al. 1988; Yeats 1988). Water from the surface of the Atlantic Ocean, deep within the Atlantic Ocean (400 m), and the Atlantic shelf contained 1.8 nM (106  $\text{ng/L}$ ), 2.7 nM (158  $\text{ng/L}$ ), and 3.5 nM (205  $\text{ng/L}$ ) nickel, respectively (van Geen et al. 1988). The mean value of nickel in surface water of the eastern Arctic Ocean is  $126\pm 54 \text{ ng/L}$  (Mart et al. 1984). Deep water samples taken at 1,500 and 2,000 m contained higher levels of nickel (220 and 230  $\text{ng/L}$ , respectively). Nickel concentrations in surface water transected on a cruise from Nova Scotia to the Sargasso Sea ranged from 117 to 329  $\text{ng/L}$ , with a median concentration of 200  $\text{ng/L}$  (Yeats 1988). Concentrations were  $\approx 2$  times higher in deep water. The nickel levels reported in

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the North Pacific and Pacific Antarctic were somewhat higher. Nickel concentration in surface water decreased slightly with increased salinity and increased with increasing phosphorus concentration. Nickel concentrations in South San Francisco Bay were about 3,000 ng/L, with one third to one-half of the nickel complexed to a class of strong organic ligands (Donat et al. 1994).

The nickel content of fresh surface water has been reported to average between 15 and 20 µg nickel/L (Grandjean 1984; NAS 1975). The concentration of dissolved nickel in the lower Mississippi River ranged from 1.2 to 1.5 µg/L in seven samples taken at different flow conditions (Shiller and Boyle 1987). In a 1977-1979 study of representative groundwaters and surface waters throughout New Jersey, in which >1,000 wells and 600 surface waters were sampled, the median nickel levels in groundwater and surface water were both 3.0 µg/L (Page 1981). The respective 90 percentile and maximum levels were 11 and 600 µg/L for groundwater and 10 and 45 µg/L for surface water. The nature of the sites with elevated nickel levels was not indicated. However, groundwater polluted with nickel compounds from a nickel-plating facility contained as high as 2,500 µg/L (IARC 1990).

Nickel concentrations from live stations in Lake Huron in 1980 had median and maximum nickel concentrations of 0.54 and 3.8 µg/L, respectively (Dolan et al. 1986). In a 1982 survey, nickel concentrations in Hamilton Harbor, Lake Ontario, ranged from <1 to 17 µg/L, with a median of 6 µg/L (Poulton 1987). The median nickel concentration from an analogous 1980 survey was 4 µg/L. Suspended sediment in surface samples (0.2 m) at Hamilton Harbor, Lake Ontario, contained 17-23 ppm nickel; samples from a depth of 20 m contained 67-87 ppm, similar to the 66 ppm of nickel found in bottom sediment samples (Poulton 1987). These findings suggest that resuspension of bottom sediment is a major contributor to the suspended sediment at 20 m depth.

Drinking water generally contains <10 µg nickel/L (Sunderman 1986). Mean levels for nickel in European drinking water range from 1 to 11 µg/L (Dabeka 1989; IARC 1990). In a 1969-1970 survey of 969 water supplies in the United States representing all water supplies in eight metropolitan areas and one state (2,503 samples), 21.7% of samples had concentrations <1 µg/L, 43.2% of the samples contained between 1 and 5 µg nickel/L, 25.6% of the samples contained between 6 and 10 µg nickel/L, 8.5% of the samples contained between 11 and 20 µg nickel/L, and 1% had levels >20 µg nickel/L (NAS 1975). In a national survey of raw, treated, and distributed water from 71 municipalities across Canada, the median nickel concentration in both treated and



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distributed provincial drinking water ranged from  $\leq 0.6$  to  $1.3 \mu\text{g/L}$  for treated water and  $1.8 \mu\text{g/L}$  for distributed water (Meranger et al. 1981). The maximum value from Sudbury, Ontario, was  $72.4 \mu\text{g/L}$ . The similarity between median and maximum values for treated and distributed water suggests that nickel is not generally picked up in the distribution system. An exception is in Quebec where the maximum nickel concentration increased from  $8.3$  to  $22.0 \mu\text{g/L}$  between the treated and distributed water. The median nickel levels in the provincial raw water ranged from  $\leq 0.6$  to  $2.3 \mu\text{g/L}$ . The maximum levels in tap waters from British Columbia, Prince Edward Island, the Yukon, and Northwest Territories were below the detection limit. The similarity in values between raw and treated water indicates that treatment methods (mainly treatment with lime, alum, or soda ash) did not remove nickel effectively.

Elevated nickel levels may exist in drinking water as a result of the corrosion of nickel-containing alloys used as valves and other components in the water distribution system as well as from nickel-plated faucets. In a Seattle study, mean and maximum nickel levels in standing water were  $7.0$  and  $43 \mu\text{g/L}$ , respectively, compared with  $2.0$  and  $28 \mu\text{g/L}$  in running water (Ohanian 1986). Although leaching of metals from pipes generally increases with decreasing pH, none of the nickel studies reported the pH of the tap water.

Several investigators reported the presence of nickel concentrations in rain. The annual mean nickel concentration in precipitation at Lewes, Delaware, was  $0.79 \mu\text{g/L}$  (Barrie et al. 1987). The mean concentration ( $\pm$  standard deviation) of nickel collected from rain showers in southern Ontario, Canada, in 1982 was  $0.56 \pm 0.07 \mu\text{g/L}$  (Chan et al. 1986). The mean concentrations in northern and central Ontario were both  $0.61 \mu\text{g/L}$ , indicating a lack of spatial variability. Sudbury, the site of a large nickel smelter, is located in central Ontario. Nickel concentrations from rain samples collected at four sites in Sweden had a mean range of  $0.017$ - $0.51 \mu\text{g/L}$  (Hansson et al 1988).

Nickel in snow from Montreal, Canada, was highly enriched compared with ambient air, ranging from  $2$  to  $300$  ppb (Landsberger et al. 1983). The nickel content of snow particulate matter was  $100$ - $500$  ppb. Nickel concentrations were highly correlated with those of vanadium, suggesting oil combustion was a source.

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### 5.4.3 Sediment and Soil

Sediment is an important sink for nickel in water. Mean nickel levels in pristine sediment from five sites off the northern coast of Alaska ranged from 25 to 31 ppm (Sweeney and Naidu 1989). Of this amount,  $\approx 10\%$  was extractable. Nickel was most highly associated with silt and clay. Background nickel concentrations in sediment cores from open water of Lake St. Clair ranged from 8.5 to 21.1 ppm, with mean concentrations of 13.6 and 17.6 ppm in sand and silty clay sediment, respectively (Rossmann 1988). The average nickel concentrations in surface sediment of four Rocky Mountain lakes ranged from 9.6 to 18 ppm (dry weight). The nickel concentrations of the five other lakes reported in the literature ranged from 6.4 to 38 ppm (Heit et al. 1984).

The range and mean nickel levels in surface sediment of Penobscot Bay, Maine, were 8.22-35.0 and 26.6 ppm (dry weight), respectively (Larsen et al. 1983). This is higher than the levels found at cleaner sites in Casco Bay in the Gulf of Maine (17.6 ppm) and Eastern Long Island (7.6 ppm) (Larsen et al. 1983). Nickel is more highly associated with fine-grained sediment with a higher organic carbon content. Levels reflect anthropogenic input as well as mineralization of the regional bedrock.

Nickel occurs naturally in the earth's crust with an average concentration of 0.0086% (86 ppm) (Duke 1980a). The nickel content of soil may vary depending on local geology. A nickel content of 0.5% (5,000 ppm) is common in podzol soil in southeastern United States, and nickel concentrations of  $>1,000$  ppm are not unusual in glacial till in southern Quebec. Both areas are underlain by ultramafic rock, which is rich in nickel. Typical nickel levels reported in soil range from 4 to 80 ppm. A soil survey by the U.S. Geological Survey throughout the United States reported that nickel concentrations ranged from  $<5$  to 700 ppm, with a geometric mean of  $13 \pm 2.31$  ppm, ranking 15th among the 50 elements surveyed (Shacklette and Boemgen 1984). In this survey, samples were taken at 20 cm at 1,318 sampling sites. Cultivated soils contain 5-500 ppm of nickel, with a typical concentration of 50 ppm (Bennett 1984). Nickel concentrations in Canadian soils are generally 5-50 ppm (Webber and Shames 1987). An extensive survey in England and Wales reported that nickel concentrations typically ranged from 4 to 80 ppm, with a median value of 26 ppm (Bennett 1984). The average farm soil in the United States contains  $>30$  ppm nickel (NAS 1975). Mean nickel concentrations in the forest floor from

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samples collected from 78 sites in nine northeastern states averaged  $11 \pm 0.8$  ppm (Friedland et al. 1986).

Nickel concentrations in contaminated soils within  $\approx 8$  km of the large nickel smelter at Sudbury, Ontario, ranged from 80 to 5,100 ppm (Duke 1980b). A study of wetland soil-sediment in Sudbury found 9,372 and 5,518 ppm of nickel at sites located 2.0 and 3.1 km from the smelter, respectively (Taylor and Crowder 1983). Nickel concentrations declined logarithmically with increasing distance from the smelter. This indicates that nickel accumulations result from atmospheric deposition and soil runoff (Taylor and Crowder 1983).

Soils from the Idaho- National Engineering Laboratory (INEL) and two background sites in southern Idaho had geometric mean nickel concentrations of 11.8-23.4 ppm dry weight; concentrations are significantly higher near INEL (Rope et al. 1988). The coal-fired steam plant that was constructed at the laboratory in 1982-1983 may be responsible for the higher nickel concentrations.

Nickel concentrations in 57 sludge-treated soils in an agricultural area of Ontario, Canada, ranged from 6.2 to 34 ppm (dry weight), with a mean of 20 ppm (Webber and Shames 1987). For 252 untreated soils, the range and mean values were 4.0-48 and 16.2 ppm, respectively. The mean for sludge-treated soil was significantly elevated.

### 5.4.4 Other Environmental Media

There have been few studies regarding the nickel content in an average diet. Nine institutional diets consisting of three meals each were analyzed for nickel (Myron et al. 1978). Four of these meals were sampled from the student center at the University of North Dakota. The remaining five diets were special diets from a rehabilitation hospital. The average nickel concentration and nickel content of the student meals ranged from 0.19 to 0.29 ppm and 140 to 221  $\mu\text{g}$ , respectively. For the hospital meals, the nickel concentration ranged from 0.21 ppm (107  $\mu\text{g}$ ) in the puree meals to 0.41 ppm (176  $\mu\text{g}$ ) in the low-calorie meal. Breakfast had the lowest nickel content. The average daily dietary nickel intake for the nine diets was  $168 \pm 11$   $\mu\text{g}$ . The average nickel concentration in the food was 0.27 ppm (dry weight). These results are comparable with estimated daily intakes of nickel of 150  $\mu\text{g}$  in Denmark, 73-142  $\mu\text{g}$  in Switzerland, and 140-150  $\mu\text{g}$  in the United Kingdom (IARC 1990; Nielsen and Flyvholm 1984). A 1962 study that used the nickel content of individual

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foods to estimate average dietary nickel intake reported intakes of 300-600 µg, which are much higher than those reported above (Grandjean 1984).

The mean nickel content of food items in the average Danish diet has been reported (IARC 1990; Nielsen and Flyvholm 1984). The ranges of mean nickel levels in various food categories (in ppm) were as follows: milk products, 0.01-0.1; meat, fish, and eggs, 0.02-0.11; vegetables, 0.04-0.52; fruits, 0.01-0.31; and grains, 0.1-1.76. The mean nickel level in meats, fruits, and vegetables is ≤0.2 ppm. The foods with the highest mean nickel content were oatmeal, spinach, asparagus, and peas. Nuts and cocoa may have nickel levels as high as 3 ppm and 10 ppm, respectively (IARC 1990). In a market basket survey completed in the United States (Pennington and Jones 1987), the highest average levels of nickel in µg/100 g were found in nuts (128.2), legumes (55), sweeteners (31.6), grains and grain products (26.2), and mixed dishes and soups (25.3).

A Canadian survey of nickel in infant formulas gave a median value of 3.53 µg/L for evaporated milk (Dabeka 1989). Different types of milk-based formulas contained from 5.8 to 28.9 µg nickel/L (Dabeka 1989). All concentrations are on a ready-to-use basis. Formulas fortified with iron had a higher nickel content. The median nickel content of soy-based formula ranged from 31.2 to 187 µg nickel/L. The average daily dietary intake of nickel by infants between the ages of 0 and 12 months could vary from 35.7 µg (4.5 µg/kg) (if evaporated milk was fed) to 74.7 µg (10.2 µg/kg) (if concentrated liquid soy-based formula was used). Infant formula (base not stated) in the United States contained an average of 0.2 µg nickel/100 g (Pennington and Jones 1987).

There is limited evidence that stainless steel pots and utensils may release nickel into acid solution (IARC 1990). Six stainless steel pots of different origins were tested to see whether they would release nickel by boiling 350 mL of 5% acetic acid in them for 5 minutes (Kuligowski and Halperin 1992). The resulting concentrations of nickel ranged from 0.01 to 0.21 ppm. Cooking acidic fruits in new stainless steel pans resulted in an increase of nickel that was about one-fifth the average daily nickel intake (Flint and Packirisamy 1995). Further use of the pans did not result in any release of nickel into the food. The use of nickel-containing catalysts in the hydrogenation of food fats may contribute to elevated nickel levels in food (Mastromatteo 1986). Grain milling may also lead to higher nickel levels (IARC 1990). The results from a recent study that attempted to identify the influence of the container on the trace metal content of preserved pork products showed no clear evidence that the metal container contributed to the metal content of the food (Brito et al.

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1990). The nickel concentration was highest in products in china and glass containers, rather than those in metal and plastic containers.

The nickel content of cigarettes is 1-3  $\mu\text{g}$ ;  $\approx 10$ -20% of this nickel is released in mainstream smoke (Sunderman 1986). This indicates that 2-12  $\mu\text{g}$  of nickel are inhaled for each pack of cigarettes smoked. Most of the nickel is in the gaseous phase, but the chemical form of the nickel is unknown (IARC 1990).

In a comprehensive survey of heavy metals in sewage sludge, 31 sludges from 23 American cities were analyzed by electrothermal atomic absorption spectroscopy (AAS) (Mumma et al. 1984). The nickel concentration in the sludges ranged from 29.0 to 800 (dry weight) and had a median value of 195 ppm. The highest concentration of nickel in sludge was in Detroit, Michigan. For comparison, the concentration of nickel in cow manure was 28.0 ppm.

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Nickel occurs naturally in the earth's crust, and the general population will be exposed to low levels of nickel in ambient air, water, and food. The average daily dietary intake of nickel in food is  $\approx 168 \mu\text{g/day}$  (Myron et al. 1978). The daily intake from drinking water is  $\approx 2 \mu\text{g}$ , assuming a median nickel concentration of 1  $\mu\text{g}$  and a consumption rate of 2 L water/day. For the highest municipal level in drinking water, which is 68  $\mu\text{g/L}$  in Sudbury, Ontario, the average daily intake of nickel would be 140  $\mu\text{g}$ . Assuming that a person inhales 20  $\text{m}^3$  air/day and the range of average nickel concentrations in U.S. cities is 5.0-49  $\text{ng/m}^3$ , the average nickel intake by inhalation would be 0.1-1.0  $\mu\text{g/day}$ . At the highest ambient nickel levels reported (917  $\text{ng/m}^3$ ), the daily inhalation intake would be 18  $\mu\text{g}$ . The nickel intake via inhalation is, therefore, a minor source of nickel to the general, nonsmoking population.

A market basket survey in England completed in 1984 estimated a dietary intake of 154-166  $\mu\text{g/day}$  or 2.2-2.4  $\mu\text{g/kg/day}$  for a 70-kg person (Smart and Sherlock 1987). Dietary intake of nickel in the United States has been estimated to range from 69  $\mu\text{g/day}$  for 6-11-month-old infants to 162  $\mu\text{g/day}$  for teenage boys, with a level of 146.2  $\mu\text{g/day}$  or 2  $\mu\text{g/kg/day}$  for a 2530-year-old male weighing 70 kg (Pennington and Jones 1987). Total nickel intake for Canadians in the general population has been estimated to range from 4.4 to 22.1  $\mu\text{g/kg/day}$ , with

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greater intake estimated for infants than for adults (CEPA 1994). Food, from which nickel is poorly absorbed, accounted for most of the intake (4.4-22 µg/kg/day). It was estimated that cigarette smoking may increase total daily intake by 0.12-0.15 µg/kg/day. Living in the vicinity of Sudbury, Ontario, where large nickel deposits are found, increased estimates of ambient air intake of nickel from about 0.0004-0.007 to 0.008 µg/kg/day and water intake of nickel from 0.005-0.16 to 0.6-2.5 µg/kg/day.

The general population is also exposed to nickel in nickel alloys and nickel-plated materials including steel, coins, and jewelry. Residual nickel may be present in soaps, fats, and oils hydrogenated with nickel catalysts (Sunderman 1986).

A NOES survey conducted by NIOSH from 1981 to 1983 estimated that 727,240 workers are potentially exposed to nickel metal, alloys, dust, fumes, salts, or inorganic nickel compounds in the United States (NIOSH 1990). Seventy percent of these estimated exposures are to nickel of an unknown molecular formula. The numbers of workers estimated to be exposed to nickel chloride, nickel oxide, and nickel sulfate are 48,717, 18,166, and 56,844, respectively. The estimate is provisional because all of the data for trade name products that may contain nickel have not been analyzed. The NOES was based on field surveys of 4,490 businesses employing nearly 1.8 million workers and was designed as a nationwide survey based on a statistical sample of virtually all workplace environments in the United States where eight or more persons are employed in all standard industrial codes except mining or agriculture. Industries with especially large numbers of potentially exposed workers include the following: plumbing, heating, air conditioning, pressed and blown glass, steel, plating and polishing, aircraft, shipbuilding, railroad, control and measuring instruments, and repair services (NIOSH 1990).

Occupational exposure to nickel will be highest for those involved in production, processing, and use of nickel. The numbers of people in the United States employed in nickel mines, smelters, and refineries at the end of 1984 were 130, 170, and 420, respectively. Primary nickel production in the United States ceased for several years in the late 1980s (Kirk 1988a). The mining and smelting operation in Riddle, Oregon, was reactivated in 1989-1990, although mining is expected to be phased out in a few years. Therefore, occupational exposure to nickel in nickel mining and primary nickel production in the United States is limited to workers in Riddle, Oregon. The concentration range of airborne nickel that workers were exposed to in laterite mining and smelting

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in Riddle, Oregon, was 4-420  $\mu\text{g nickel}/\text{m}^3$  (Warner 1984). This is currently the only nickel and smelting operation in the United States. The ranges of airborne nickel concentrations reported for other industries are as follows: stainless steel production,  $<1\text{-}189 \mu\text{g}/\text{m}^3$ ; high nickel alloy production,  $1\text{-}4.4 \mu\text{g}/\text{m}^3$ ; foundry operations, from not detectable to  $900 \mu\text{g}/\text{m}^3$ ; electroplating, from  $<2$  to  $<16 \mu\text{g}/\text{m}^3$ ; nickel-cadmium battery manufacture,  $20\text{-}1,910 \mu\text{g}/\text{m}^3$ ; nickel catalyst production from nickel sulfate,  $1\text{-}1,240 \mu\text{g}/\text{m}^3$ ; production of nickel salts from nickel or nickel oxide,  $9\text{-}590 \mu\text{g}/\text{m}^3$ ; and production of wrought nickel and alloys from metal powder,  $1\text{-}60,000 \mu\text{g}/\text{m}^3$  (Warner 1984). Average nickel concentrations for selected work areas or operations in these industries, other than producing wrought nickel and alloys from metal powder, range from  $<3$  to  $378 \mu\text{g}/\text{m}^3$ ; for wrought nickel and alloy production from metal powder, the average concentration is  $1,500 \mu\text{g}/\text{m}^3$ . Operations that produce the highest levels of airborne nickel are those that involve grinding, welding, and handling powders. Not only do occupational exposures vary widely among these operations and industries, but the form of nickel that workers are exposed to varies. Because sulfur has a deleterious effect on many metals and alloys, nickel sulfate and sulfidic nickel compounds are generally not found in metallurgical workplaces (Warner 1984). Nickel subsulfide is known to exist in only one application in nickel-using industries, namely in certain spent catalysts. Nickel oxide is used as a raw material in steel production, and oxide fumes and dust may occur in melting, casting, and welding operations. There are probably more exposures to metallic nickel in nickel-using industries than in nickel-producing industries. These occur during powder handling, grinding, and polishing operations and in casting operations.

Nickel is an essential trace element for animals (Sunderman 1986), and a 70-kg reference man contains 10 mg of nickel, giving an average body concentration of 0.1 ppm (Iyengar 1986). The highest tissue concentrations of nickel are found in the lungs of nickel smelting and refinery workers. The highest nickel concentration reported in lung tissue of 39 nickel refinery workers autopsied in 1978-1984 was 1,344 ppm (dry weight), compared to 1.7 ppm in unexposed persons (Andersen and Svenes 1989).

Ten studies of nickel in human milk gave disparate results. Six median values ranged from 5 to  $16 \mu\text{g}/\text{L}$ , and 10 mean values ranged from 1.5 to  $39 \mu\text{g}/\text{L}$  (Iyengar 1989). Five of the six medians ranged from 11 to  $16 \mu\text{g}/\text{L}$ . The lowest and highest mean values were from Finland and Germany GDR, respectively. None of the studies were from the United States. Individual values ranged from 0 to  $130 \mu\text{g nickel}/\text{L}$ .

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Serum nickel levels in hospital workers averaged  $0.6 \pm 0.3$   $\mu\text{g/L}$  in Sudbury, Ontario, versus  $0.2 \pm 0.2$   $\mu\text{g/L}$  in Hartford, Connecticut (Hopfer et al. 1989). Measurements of nickel content of tap water in these communities were reported as  $109 \pm 46$  and  $0.4 \pm 0.2$   $\mu\text{g/L}$ , respectively (Hopfer et al. 1989). Concentrations of nickel in the blood and urine of workers at a rolling mill in Poland were  $18.5 \pm 4.0$  and  $25.7 \pm 5.1$   $\mu\text{g/L}$ , respectively (Baranowska-Dutkiewicz et al. 1992). Nickel concentrations in the urine of preschool children in Poland were  $10.6 \pm 4.1$  and  $9.4 \pm 4.7$   $\mu\text{g/L}$  for children from an industrial region and a health resort, respectively (Baranowska-Dutkiewicz et al. 1992). After reviewing studies of nickel concentrations in humans, Templeton et al. (1994) indicated that the most reliable reference values were 0.2  $\mu\text{g/L}$  for nickel in serum of healthy adults and 1-3  $\mu\text{g/L}$  for nickel in urine. These values are dependent on food and fluid intake and environmental factors. Fewer studies of nickel in whole blood were identified, and a reference value was not suggested.

Fingernail samples from 71 Americans contained 0.57 ppm of nickel; samples from residents of Japan, India, Canada, and Poland had nickel concentrations that ranged from 1.1 to 3.9 ppm (Takagi et al. 1988). Nickel levels are higher in males than in females. Higher levels occur in younger people and decrease with age. The mean concentration of nickel in hair samples from 55 men and women from Scranton, Pennsylvania, was 1.01 ppm; populations from cities in Japan, India, Canada, and Poland had mean nickel levels between 0.26 and 2.70 ppm (Takagi et al. 1986). A more recent National Health and Nutritional Examination Survey II of hair from a random sample of 271 adults, ages 20-71, from three communities had geometric mean and median nickel levels of 0.39 and 0.45 ppm, respectively. Ten percent of the group had nickel levels  $>1.50$  ppm (DiPietro et al. 1989).

The nickel content of most natural vegetation is 0.05-5 ppm on a dry weight basis (NAS 1975). Near source areas, nickel on plants may be elevated because of direct foliar deposition. Some species of plants have the ability to hyperaccumulate nickel (Brooks 1980). The concentration in the leaves of *Alyssum bertolonii* contained 120 ppm nickel (12%). These plants are thought to produce organic ligands that complex with nickel.

The modal concentration of nickel in 159 species of edible fin fish from the U.S. National Marine Fisheries Survey was 0.2-0.3 ppm (wet weight) (Heit et al. 1989). Jenkins (1980) has compiled literature concentrations of nickel levels in aquatic species. The ranges of nickel concentrations in



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freshwater fish, marine fish, and mollusks from areas thought to be uncontaminated are from <0.2 to 2.0, from 0.0 to  $\approx$ 4.0, and from 0.4 to 2.0 ppm (wet weight), respectively. The highest levels found near sources of pollution, especially near nickel smelters, were 51.6 ppm for freshwater fish and 191.0 ppm for mollusks. The nickel content of muscle tissue of several fish species collected from metal-contaminated lakes near Sudbury, Ontario, was below the detection limit (2.0 ppm dry weight), except for two of four yellow perch, which had levels of 2.8 and 3.4 ppm (Bradley and Morris 1986). A more recent survey of metals in stocked lake trout in live lakes near Sudbury, Ontario, reported that concentrations of metal in trout muscle were not significantly different from those in the hatchery (0.34-0.83 ppm wet weight versus 0.49 ppm) (Bowlby et al. 1988). Nickel concentrations in the lower Savannah River and Savannah National Wildlife Refuge in Georgia were higher than those reported above for uncontaminated areas. These levels were consistently higher in gar (2.35-6.67 ppm wet weight) than in catfish (0.37-1.41 ppm) (JVinger et al. 1990). As part of the National Status and Trends Program for Marine Environmental Quality, the concentration of nickel in oysters and mussels was investigated (NOAA 1987). The nickel concentration in bivalve tissue collected in 1986 ranged from 0.55 to 12.57 ppm (dry weight). The highest tissue concentration was found in Matagorda Bay, Texas, and the second highest concentration, 6.57 ppm, was found in both Tomales Bay, California, and Chesapeake Bay, Maryland. Oysters around three coastal marinas in South Carolina with sediment nickel levels of 25.8-40.8 ppm (dry weight) had levels of 0.3-5.2 ppm (Marcus and Thompson 1986). Mean nickel levels in oysters at four sites in the Mississippi Sound varied from <0.5 to 4.7 ppm (wet weight) (Lytle and Lytle 1990).

### 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing nickel exposure, it is important to consider what form of nickel a person is exposed to and its bioavailability. Such information is not often available. Although high concentrations of nickel may be found in contaminated soil and sediment, it may be embedded in a crystalline matrix or bound to hydrated iron, aluminum, and manganese oxides and, therefore, not bioavailable.

Nickel-containing alloys are used in patients in joint prostheses, sutures, clips, and screws for fractured bones. Corrosion of these implants may lead to elevated nickel levels in the surrounding tissue and to the release of nickel into extracellular fluid (IARC 1990; Sunderman 1989a; Sunderman et al. 1986, 1989c). Serum albumin solutions used for intravenous infusion fluids have

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been reported to contain as much as 222 µg nickel/L. Dialysis fluid has been reported to contain as much as 0.82 µg nickel/L. Patients receiving transfusions or dialysis may be exposed to high levels of nickel.

People who live near or work at facilities that produce stainless steel and other nickel-containing alloys, oil-fired power plants, coal-fired power plants, and refuse incinerators may be exposed to high levels of nickel in airborne dust, soil, and vegetation. People who live near or work at waste sites that receive waste from nickel-producing or using industries or that handle bottom ash or fly ash from power plants or refuse incinerators may also be exposed to higher levels of nickel. Exposure would result from inhalation, dermal contact, or ingestion of contaminated soil or vegetation. It is possible that nickel from waste sites will contaminate groundwater. This situation is most probable with electroplating waste. People using this groundwater may be exposed to high nickel concentrations.

### 5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of nickel is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of nickel.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

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### 5.7.1 Identification of Data Needs

**Physical and Chemical Properties.** Except for differences between black and green nickel oxide, the physical and chemical properties of nickel and its compounds reported in Table 3-2 (HSDB 1996) have been adequately characterized.

**Production, Import/Export, Use, and Release and Disposal.** Information on the production, import, export, and use of nickel metal and nickel alloys is readily available (Chamberlain 1985; Kirk 1988a, 1988b; NTD 1996; Tien and Howson 1981). However, information on the production, import, and use patterns of other nickel compounds is not generally available and is needed to assess human exposure to these compounds. Except for recycling of metal scrap, little information is available regarding the disposal of nickel and its compounds.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1993, became available in May of 1995. This database will be updated yearly and provides a list of industrial production facilities and emissions.

Releases according to the TRI database are reported in Table 5-1 (TR193 1995). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list. Much of the nickel released to the environment is transferred off-site for disposal and probably landfilled. Nickel wastes from former mining and smelting operations may have been discarded in large tailing piles. Acid conditions are often created in tailing piles from sulfidic ores that increase the potential for leaching (Wood 1987). This is not the case with lateritic deposits such as those found in Riddle, Oregon. Information regarding nickel leaching from slag heaps is important in assessing releases to the environment. More detailed information regarding disposal methods and the form of nickel disposed of is necessary to assess potential nickel exposure.

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**Environmental Fate.** Nickel is an element and therefore, is not destroyed in the environment. In assessing human exposure, one must consider the form of nickel and its bioavailability. This information is site specific. Data regarding the forms of nickel in air, soil, and sediment are fragmentary and inadequate (Sadiq and Enfield 1984a; Schroeder et al. 1987). Also lacking is adequate information on the transformations that may occur, the transformation rates, and the conditions that facilitate these transformations. Information relating to the adsorption of nickel by soil and sediment is not adequate. In some situations, adsorption appears to be irreversible. In other situations, however, adsorption is reversible. More data would be helpful in detailing those situations where adsorbed nickel may be released and those where release is unlikely.

**Bioavailability from Environmental Media.** The absorption and distribution of nickel as a result of inhalation, ingestion, and dermal exposure are discussed in Sections 2.3.1 and 2.3.2. Quantitative data relating the physical/chemical properties of nickel (e.g., particle size, chemical forms of nickel) with its bioavailability are available for inhaled nickel. In aqueous media, nickel is in the form of the hexahydrate ion, which is poorly absorbed by most living organisms (Sunderman and Oskarsson 1991). Additional studies which examine the absorption of nickel from soil would be useful.

**Food Chain Bioaccumulation.** Data are available on the bioconcentration of nickel in fish and aquatic organisms (Birge and Black 1980; Callahan et al. 1978; Zaroogian and Johnson 1984). Higher levels of nickel have been found in gar compared with catfish from the same environment (Winger et al. 1990). More data on different species of fish at different sites would be useful in explaining these results. Data are limited on the nickel levels in wild birds and mammals (Alberici et al. 1989; Dressler et al. 1986; Jenkins 1980). A larger database including information on both herbivorous and carnivorous species living in both polluted and unpolluted environments is desirable in establishing whether nickel biomagnification in the food chain occurs under some circumstances.

**Exposure Levels in Environmental Media.** Reliable monitoring data for the levels of nickel in contaminated media at hazardous waste sites are needed so that the information obtained on levels of nickel in the environment can be used in combination with the known body burden of nickel to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Representative and recent monitoring data for nickel in air, water, and foods are essential for estimating the extent of exposure from each of these sources. Nickel levels in

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environmental media are often below the detection limit of the analytical method employed. When a substantial fraction of determinations of nickel levels in environmental samples are below the detection limit, an arithmetic mean may not adequately represent the data. Although data on the levels of nickel in ambient air are available (EPA 1986a; Evans et al. 1984; Kowalczyk et al. 1982; Lioy et al. 1987; Salzman et al. 1985; Wiersema et al. 1984), these data are not recent enough for estimating the current levels of exposure to nickel by the U.S. population via inhalation. This is especially important since emission controls are being increasingly mandated for industry, power generators, and incinerators. Similarly the last comprehensive survey of nickel in U.S. drinking water is for 1969-1970 (NAS 1975). Information on nickel in the U.S. diet is limited to one study from North Dakota (Myron et al. 1978). While results from this study are in agreement with ones from Europe (IARC 1990), information covering a larger geographic area in the United States is desirable. Few data are available regarding nickel levels at contaminated or hazardous waste sites (Bradley and Morris 1986; Duke 1980b; Taylor and Crowder 1983). This information is necessary for exposure assessment analysis at these sites. Since nickel is found in all soil, studies should focus on waste sites where nickel levels are substantially above those found in ordinary soil.

**Exposure Levels in Humans.** This information is necessary for assessing the need to conduct health studies on these populations. The nickel levels in body fluids, tissue, hair, nails, and breast milk are available (DiPietro et al. 1989; Hopfer et al. 1989; IARC 1990; Iyengar 1989; Takagi et al. 1986, 1988). Serum and urine levels in some exposed workers have also been published (Angerer and Lehnert 1990; Bencko et al. 1986; Bemacki et al. 1978; Elias et al. 1989; Ghezzi et al. 1989; Hassler et al. 1983; Morgan and Rouge 1984; Torjussen and Andersen 1979). These data do not refer to populations living around the hazardous waste sites that contain elevated levels of nickel. Additional studies which examine nickel levels in body fluids and tissues from persons living near hazardous waste sites that contain elevated levels of nickel would be useful.

**Exposure Registries.** Although there is no U.S. exposure registry for nickel, a Finnish exposure registry for occupational carcinogens exists and this registry contains information on nickel and inorganic nickel compounds (Grandjean 1984). This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the

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epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

### **5.7.2 On-going Studies**

A number of on-going studies concerning the fate and transport of nickel were identified in the CRIS (1994) and FEDRIP (1994) databases. J. Sims will be measuring nickel content in the soil of commercial crop soil samples and comparing nickel concentrations with soil properties. A number of investigators will be examining the fate of nickel in sludge applied to agricultural fields (T. Logan, J.R. Preer) and forest and nonagricultural land (F. Dixon, A.O. McCullough).